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(54) ELECTRICALLY CONDUCTIVE WHITE POWDER AND ITS MANUFACTURE

(57)Abstract:
PURPOSE: To provide white conductive powder which is extremely low in volume resistivity and extremely high in whiteness and does not contain virulent antimony.
CONSTITUTION: White conductive powder has a double conductive cover layer, which is composed of a tin dioxide layer as a lower layer and an indium oxide layer containing tin dioxide as an upper layer, on the surface of a white inorganic pigment particle. This white conductive powder can be gotten by equally deposing hydrolytic reaction products of tin on the surface of a white inorganic pigment particle first, and subsequently, covering it with a hydrate of indium oxide, which contains tin dioxides 1-20wt.%, and further, heat-treating it at 350-750°C in nonoxidative atmosphere.

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CLAIMS

[Claim(s)]
[Claim 1] White conductivity powder characterized by having the conductive enveloping layer which a

lower layer is a layer of diacid-ized tin and is a layer of the indium oxide in which the upper layer contains diacid-ized tin on the front face of a white inorganic pigment particle.

[Claim 2] White conductivity powder according to claim 1 chosen from the group which a white inorganic pigment particle becomes from a titanium dioxide, an aluminum oxide, a silicon dioxide, a zinc oxide, a barium sulfate, a zirconium dioxide, a titanic-acid alkali-metal salt, and a muscovite.

[Claim 3] The hydrate of diacid-ized tin is made to cover 0.5 to 50% of the weight as SnO2 to a pigment to a white inorganic pigment particle front face. Subsequently, the hydrate of the indium oxide which sets the hydrate of diacid-ized tin to SnO2, and contains it 0.1 to 20% of the weight is made to cover five to 200% of the weight as In 2O3 to a pigment. Furthermore, the manufacture approach of the white conductivity powder according to claim 1 characterized by heat-treating at 350-750 degrees C according to a non-oxidizing atmosphere.

[Claim 4] The manufacture approach of the white conductivity powder according to claim 3 characterized by performing heat-treatment, blowing inert gas.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention -- antistatic -- it is related with white conductivity powder probably used in the fields, such as a coating, plastics, fiber, etc. of business, and a resistance regulator of the electrification regulator and photoconductor drum of the toner for electrophotography.

[0002]

[Description of the Prior Art] Although carbon black and the metal powder which are used so much as an electrical conducting material had dramatically low volume resistivity and being excelled in property now, since those color tones were black, the application was limited. The manufacturing method of the conductive white titanium oxide which covered the tin oxide which doped antimony as the cure as what covered the front face of a titanium dioxide with the stannic oxide (JP,53-92854,A official report), or its conductive amelioration article was indicated (JP,58-209002,A official report etc.).

[0003] antistatic [using this white conductivity titanium oxide] -- the coating of business, plastics, and fiber have been increasing need in recent years taking advantage of the advantage of white to the white robe which needs feeling of purity, the inner package of a clean room, or the coating and plastic of ******.

[0004] However, it came to talk about the problem on the toxicity of antimony recently, and development of the white conductivity powder which does not contain antimony is needed. As a process which does not use antimony, although for example, the JP,4-154621,A official report was indicated, although antimony is not contained, by this approach, the thing equivalent to that in which volume resistivity contained antimony is not obtained.

[0005] Moreover, although the potassium titanate covered with the indium oxide containing diacid-ized tin was indicated in the JP,61-141618,A official report, since the water solution of indium chloride and the ethanol solution of a stannous chloride were used separately and both coat rate did not become homogeneity, there was a problem that volume resistivity was not stabilized. Furthermore, since the base acted as an impurity to which the conductivity of an enveloping layer is reduced, in spite of having made [many] the amount of coats of the indium oxide containing diacid-ized tin, the volume resistivity of fine particles was as high [the coat condition of the indium oxide to the potassium titanate particle front face of a base was bad, and] as 104 ohm-cm.

[0006] Moreover, although the muscovite covered with the indium oxide containing diacid-ized tin was indicated in the JP,60-253112,A official report, like the case of potassium titanate, the coat condition of

indium oxide was bad and needed to make [many] the amount of coats of the indium oxide which has the influence of a base and contains diacid-ized tin.

[0007] Since it could be difficult to make homogeneity cover the coat of the indium oxide which contains diacid-ized tin also in other white inorganic pigment particles and it was not able to reduce volume resistivity under the effect of the inorganic pigment particle of a base, conductive good white conductivity powder was not obtained.

[0008]

[Problem(s) to be Solved by the Invention] Although this invention does not use antimony with a toxic problem, its white degree is high and it tends to offer the white conductivity powder which has the outstanding conductivity.

[0009]

[Means for Solving the Problem] this invention persons complete this invention, as a result of repeating research wholeheartedly in order to develop the white powder which has conductivity equivalent to an antimony content article in spite of having not used antimony with a toxic problem, maintaining white degree. That is, this invention provides a white inorganic pigment particle front face with the white conductivity powder which a lower layer is a layer of diacid-ized tin and is characterized by having the conductive enveloping layer which is a layer of the indium oxide in which the upper layer contains diacid-ized tin.

[0010] The white conductivity powder concerning this invention makes a white inorganic pigment particle front face cover the hydrate of 0.5 - 50% of the weight of diacid-ized tin to homogeneity as SnO2 to a pigment. Succeedingly It is made to cover five to 200% of the weight to a pigment by setting to In 2O3 the hydrate of the indium oxide which sets the hydrate of diacid-ized tin to SnO2, and contains it 0.1 to 20% of the weight, and is obtained by heat-treating at 350-750 degrees C according to a non-oxidizing atmosphere further.

[0011] If the white inorganic pigment particle used as the base of this invention is a titanium dioxide, an aluminum oxide, a silicon dioxide, a zinc oxide, a barium sulfate, a zirconium dioxide, a commercial titanic-acid alkali-metal salt, or a commercial muscovite, it can use either. If it explains to a detail more taking the case of a titanium dioxide, there is no limit in the magnitude of a particle, and an anatase mold, a rutile mold, and an amorphous thing can also use the thing of any spherical and needlelike configurations as crystal form further. In addition, although this invention thought white as important, it is applicable also to various colored pigments, such as an iron oxide.

[0012] Next, explanation about the progress which completed the white conductivity powder by this invention is given.

[0013] In order to give conductivity to a white inorganic pigment, how to cover directly as an approach of covering the hydrate of the indium oxide containing the hydrate of diacid-ized tin on a particle front face was examined first. However, good conductivity was not acquired, even if it could not make an inorganic pigment particle front face cover the hydrate of indium oxide with this approach to homogeneity and having been heat-treated under the effect of the inorganic pigment particle of a base. Then, in order to solve this problem, as a result of continuing examination, it became clear that a uniform coat could be formed by observation by the transmission electron microscope by covering with the form of a hydrate the metallic oxide usually used considering the front face of the inorganic pigment particle of a base as coating materials, such as an aluminum oxide, and a zinc oxide, a zirconium dioxide, and covering the hydrate of the indium oxide which contains the hydrate of diacid-ized tin succeedingly. However, these metallic oxides were still insufficient for obtaining a good conductive thing under the effect of the hydrate of a substrate. Then, as a result of making a substrate into the hydrate of the tin oxide, it becomes clear that the powder in which effect from the hydrate of the inorganic pigment particle of a base and the tin oxide of a substrate is not received. but very good conductivity is shown is obtained, and it came to complete this invention. In addition, even if the hydrate of a small amount of indium oxide is

mixing into the hydrate of lower layer diacid-ized tin in the range which does not spoil the effectiveness of this invention, it does not interfere.

[0014] Detailed explanation of the manufacture approach in this invention will be given succeedingly.

[0015] There are various approaches as an approach of making the coat of the hydrate of lower layer diacid-ized tin forming. For example, after adding the solution of tin<4> salt or a stannate to the water suspension of a white inorganic pigment, the approach of adding independently in parallel the approach, the tin<4> salt or the tin hydrochloric acid which adds alkali or an acid, alkali, or an acid, and carrying out coat processing etc. is in it. for carrying out coat processing of the hydrated compound of the tin oxide on a white inorganic pigment particle front face at homogeneity -- the approach of the latter concurrency addition -- more -- suitable -- **** -- this time -- water suspension -- 50-100 degrees C -- warming -- holding is more desirable. Moreover, pH at the time of carrying out concurrency addition of tin<4> salt or a stannate, alkali, or the acid is set to 2-9. Since the isoelectric point of a diacid-ized tin hydrate is pH=5.5, it can be important to maintain pH=2-5 or pH 6-9 preferably, and, thereby, it can make a white inorganic pigment particle front face carry out the deposition of the hydration product of tin to homogeneity.

[0016] As tin<4> salt, tin chloride, sulfuric-acid tin, nitric-acid tin, etc. can be used, for example. Moreover, as a stannate, stannic-acid sodium, a stannic-acid potassium, etc. can be used, for example.

[0017] As alkali, a sodium hydroxide, a potassium hydroxide, a sodium carbonate, potassium carbonate, an ammonium carbonate, aqueous ammonia, ammonia gas, etc. can use a hydrochloric acid, a sulfuric acid, a nitric acid, an acetic acid, etc. as an acid, for example.

[0018] The amount of coats of the hydrate of diacid-ized tin is 0.5 - 50 % of the weight as SnO_2 to the white inorganic pigment of a base, and is 1.5 - 40 % of the weight preferably. If too few, the coat condition of the hydrate of the indium oxide containing the tin oxide covered upwards becomes uneven, and moreover, the volume resistivity of fine particles will become high in response to the effect of the inorganic pigment of a base. If many [too], the amount of the hydrate of the tin oxide which has not been stuck to the inorganic pigment particle front face of a base will increase, and a coat will tend to become an ununiformity.

[0019] Next, although the approach of making the coat of the hydrate of the indium oxide containing the upper diacid-ized tin forming also has various approaches, in order not to dissolve the coat of the hydrate of the diacid-ized tin covered previously, the method of adding independently the mixed solution and alkali of tin<4> salt and an indium salt in parallel, and making a coat form is more desirable. At this time, it is more desirable to warm water suspension at 50-100 degrees C. Moreover, pH at the time of carrying out concurrency addition of a mixed solution and the alkali is set to 2-9, it can be important to maintain by pH 2-5 or pH 6-9 preferably, and, thereby, it can carry out the deposition of tin and the hydration product of an indium to homogeneity.

[0020] As a raw material of tin, tin chloride, sulfuric-acid tin, nitric-acid tin, etc. can be used, for example. As a raw material of an indium, indium chloride, indium sulfate, etc. can be used, for example.

[0021] To In_2O_3, even if a diacid-ized tin addition is 2.5 - 15 % of the weight preferably 0.1 to 20% of the weight as SnO_2, and there are and there are, desired conductivity is not acquired. [too many] [too few]

[0022] Even if desired conductivity will not be acquired to the inorganic pigment of a base if it is 8 - 150 % of the weight preferably five to 200% of the weight and is too few as In_2O_3, but there are too many throughputs of indium oxide, conductivity hardly improves, and becomes expensive and is not desirable from a cost side.

[0023] In addition, in this detail, "conductive" powder means what has the value of 1 - 500 ohm-cm as a volume resistivity value of fine particles. As the example mentioned later is shown, the white conductivity powder which says 100 or less ohm-cm comparable as an antimony content article by this invention, and it says is 10 or less ohm-cm by the case and which was dramatically excellent in conductivity can be obtained.

[0024] In case it heat-treats, it is desirable to carry out according to a non-oxidizing atmosphere at 350-750 degrees C, and it can make low triple [2-] figures volume resistivity of fine particles compared with what was heat-treated in air.

[0025] Inert gas can be used in order to consider as a non-oxidizing atmosphere. As inert gas, nitrogen, helium, an argon, carbon dioxide gas, etc. can be used. Heat-treating industrially, blowing nitrogen gas is advantageous in cost, and that by which the property was stabilized is obtained.

[0026] Preferably, the temperature at the time of heating is 400-700 degrees C, and 350-750 degrees C of desired conductivity cannot acquire it easily, also when lower [than this range] and high. Moreover, since heating time cannot desire effectiveness beyond it even if there is no heating effectiveness and it is too long, when too brief, 15 minutes - about 4 hours are suitable for it, and it is about 1 - 2 hours preferably.

[0027] An example is given to below and this invention is further explained to a detail. The following examples are not described only for instantiation and the range of invention is not restricted by these.

[0028] 1l. of water was made to distribute 100g (Titan Kogyo KR-310 and specific-surface-area [of 7m] 2/g) of example 1 rutile titanium dioxides, and it considered as water suspension. this suspension -- 70 degrees C -- warming -- it held. It applied for about 40 minutes and simultaneous adding of the solution and 12-% of the weight aqueous ammonia which melted 11.6g (SnCl4and5H2O) of stannic chlorides prepared separately to 100ml of 2-N hydrochloric acids was carried out for pH of suspension so that it might hold to 7-8. Simultaneous dropping of the solution and 12-% of the weight aqueous ammonia which melted 36.7g (InCl3) of indium chloride and 5.4g (SnCl4and5H2O) of stannic chlorides prepared separately succeedingly to 450ml of 2-N hydrochloric acids was carried out over about 1 hour so that pH of suspension might be held to 7-8. After dropping termination, processing suspension was filtered, it washed, and the cake of the obtained processing pigment was dried at 110 degrees C.

[0029] Subsequently, the obtained desiccation powder was heat-treated at 500 degrees C in the nitrogen gas air current (a part for 1l./) for 1 hour, and the white conductivity powder made into the object was obtained.

[0030] Powdered volume resistivity was 3.9 ohm-cm. Moreover, the coat condition on the front face of a particle was very uniform as shown in the transmission electron microscope photograph of (drawing 1).

[0031] In example 2 example 1, instead of the rutile titanium dioxide, the aluminum oxide (Sumitomo Chemical AKP-30 and specific-surface-area [of 6m] 2/g) was used, and 11.6g of stannic chlorides was set to 16.2g, and also it processed like the case of this example, and the white conductivity powder made into the object was obtained. The volume resistivity of fine particles was 8.2 ohm-cm.

[0032] In example 3 example 1, the zinc oxide (Mitsui Mining & Smelting zinc white) was used instead of the rutile titanium dioxide, and the white conductivity powder which 16.2g, 36.7g of indium chloride, and 5.4g of stannic chlorides were set to 51.3g and 13.3g, respectively, and also processes 11.6g of stannic chlorides like the case of this example, and targets them was obtained. The volume resistivity of fine particles was 39 ohm-cm.

[0033] In example 4 example 1, the white conductivity powder which used the barium sulfate (product B-50 made from the Sakai chemistry) instead of the rutile titanium dioxide, and 36.7g of indium chloride and 5.4g of stannic chlorides were set to 23.2g and 4.7g, respectively, and also processes like the case of this example, and is made into the object was obtained. The volume resistivity of fine particles was 47 ohm-cm.

[0034] In example 5 example 1, potassium titanate (Titan Kogyo HT-300 and specific-surface-area [of 3m] 2/g) was used instead of the rutile titanium dioxide, 36.7g of indium chloride and 5.4g of stannic chlorides were set to 31.9g and 4.7g at 6.0g, respectively, and also 11.6g of stannic chlorides was processed like the case of this example, and the white conductivity powder made into the object was obtained. The volume resistivity of fine particles was 87 ohm-cm.

[0035] In example 6 example 1, an anatase mold ultrafine particle titanium dioxide (Titan Kogyo

STT-65C and specific-surface-area 60m2/g) is used instead of a rutile titanium dioxide. The solution which melted 11.6g of stannic chlorides to 100ml of 2-N hydrochloric acids In the solution which melted 39.8g of stannic chlorides to 300ml of 2-N hydrochloric acids Moreover, the solution which melted 36.7g of indium chloride, and 5.4g of stannic chlorides to 450ml of 2-N hydrochloric acids It considered as the solution which melted 159.6g of indium chloride, and 23.5g of stannic chlorides to 1000ml of 2-N hydrochloric acids, and also it processed like the case of this example, and the white conductivity powder made into the object was obtained. The volume resistivity of fine particles was 42 ohm-cm.
[0036] In example 7 example 1, everything but having used the muscovite (Kuraray SUZORAITO mica and specific-surface-area 7m2/g) instead of the rutile titanium dioxide was processed like the case of this example, and obtained the white conductivity powder made into the object. The volume resistivity of fine particles was 22 ohm-cm.
[0037] example 8 example 1 -- setting -- instead of [of a rutile titanium dioxide] -- a zirconium dioxide (the high intensity zirconia made from Oriental soda --) Specific-surface-area of 17m 2/g is used. 11.6g of stannic chlorides to 23.2g Moreover, the solution which melted 36.7g of indium chloride, and 5.4g of stannic chlorides to 450ml of 2-N hydrochloric acids It considered as the solution which melted 73.4g of indium chloride, and 10.8g of stannic chlorides to 900ml of 2-N hydrochloric acids, and also it processed like the case of this example, and the white conductivity powder made into the object was obtained. The volume resistivity of fine particles was 32 ohm-cm.
[0038] In example of comparison 1 example 1, except not performing processing with the solution which melted 11.6g of stannic chlorides to 100ml of 2-N hydrochloric acids, it processed like the case of this example and white conductivity powder was obtained. The volume resistivity of fine particles was dramatically as high as 3.9x105 ohm-cm, and there was much what separated from the base like the transmission electron microscope photograph which also showed the coat condition on the front face of a particle to (drawing 2).
[0039] In example of comparison 2 example 1, everything but carrying out in air instead of heat-treating in a nitrogen gas air current was processed like the case of this example, and obtained white powder. The volume resistivity of fine particles was very as high as 4.3x103 ohm-cm.
[0040]
[Effect of the Invention] This invention manufactures comparatively easily the conductive high powder of the whiteness degree excellent in the conductivity which can be used for various fields, without using antimony with the problem on toxicity, and has a high advantage industrially.

TECHNICAL FIELD

[Industrial Application] this invention -- antistatic -- it is related with white conductivity powder probably used in the fields, such as a coating, plastics, fiber, etc. of business, and a resistance regulator of the electrification regulator and photoconductor drum of the toner for electrophotography.

PRIOR ART

[Description of the Prior Art] Although carbon black and the metal powder which are used so much as an electrical conducting material had dramatically low volume resistivity and being excelled in property now, since those color tones were black, the application was limited. The manufacturing method of the conductive white titanium oxide which covered the tin oxide which doped antimony as the cure as what covered the front face of a titanium dioxide with the stannic oxide (JP,53-92854,A official report), or its conductive amelioration article was indicated (JP,58-209002,A official report etc.).

[0003] antistatic [using this white conductivity titanium oxide] -- the coating of business, plastics, and fiber have been increasing need in recent years taking advantage of the advantage of white to the white robe which needs feeling of purity, the inner package of a clean room, or the coating and plastic of ******.

[0004] However, it came to talk about the problem on the toxicity of antimony recently, and development of the white conductivity powder which does not contain antimony is needed. As a process which does not use antimony, although for example, the JP,4-154621,A official report was indicated, although antimony is not contained, by this approach, the thing equivalent to that in which volume resistivity contained antimony is not obtained.

[0005] Moreover, although the potassium titanate covered with the indium oxide containing diacid-ized tin was indicated in the JP,61-141618,A official report, since the water solution of indium chloride and the ethanol solution of a stannous chloride were used separately and both coat rate did not become homogeneity, there was a problem that volume resistivity was not stabilized. Furthermore, since the base acted as an impurity to which the conductivity of an enveloping layer is reduced, in spite of having made [many] the amount of coats of the indium oxide containing diacid-ized tin, the volume resistivity of fine particles was as high [the coat condition of the indium oxide to the potassium titanate particle front face of a base was bad, and] as 104 ohm-cm.

[0006] Moreover, although the muscovite covered with the indium oxide containing diacid-ized tin was indicated in the JP,60-253112,A official report, like the case of potassium titanate, the coat condition of indium oxide was bad and needed to make [many] the amount of coats of the indium oxide which has the influence of a base and contains diacid-ized tin.

[0007] Since it could be difficult to make homogeneity cover the coat of the indium oxide which contains diacid-ized tin also in other white inorganic pigment particles and it was not able to reduce volume resistivity under the effect of the inorganic pigment particle of a base, conductive good white conductivity powder was not obtained.

EFFECT OF THE INVENTION

[Effect of the Invention] This invention manufactures comparatively easily the conductive high powder of the whiteness degree excellent in the conductivity which can be used for various fields, without using antimony with the problem on toxicity, and has a high advantage industrially.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] Although this invention does not use antimony with a toxic problem, its white degree is high and it tends to offer the white conductivity powder which has the outstanding conductivity.

MEANS

[Means for Solving the Problem] this invention persons complete this invention, as a result of repeating research wholeheartedly in order to develop the white powder which has conductivity equivalent to an antimony content article in spite of having not used antimony with a toxic problem, maintaining white degree. That is, this invention provides a white inorganic pigment particle front face with the white conductivity powder which a lower layer is a layer of diacid-ized tin and is characterized by having the conductive enveloping layer which is a layer of the indium oxide in which the upper layer contains

diacid-ized tin.

[0010] The white conductivity powder concerning this invention makes a white inorganic pigment particle front face cover the hydrate of 0.5 - 50% of the weight of diacid-ized tin to homogeneity as SnO2 to a pigment. Succeedingly It is made to cover five to 200% of the weight to a pigment by setting to In 2O3 the hydrate of the indium oxide which sets the hydrate of diacid-ized tin to SnO2, and contains it 0.1 to 20% of the weight, and is obtained by heat-treating at 350-750 degrees C according to a non-oxidizing atmosphere further.

[0011] If the white inorganic pigment particle used as the base of this invention is a titanium dioxide, an aluminum oxide, a silicon dioxide, a zinc oxide, a barium sulfate, a zirconium dioxide, a commercial titanic-acid alkali-metal salt, or a commercial muscovite, it can use either. If it explains to a detail more taking the case of a titanium dioxide, there is no limit in the magnitude of a particle, and an anatase mold, a rutile mold, and an amorphous thing can also use the thing of any spherical and needlelike configurations as crystal form further. In addition, although this invention thought white as important, it is applicable also to various colored pigments, such as an iron oxide.

[0012] Next, explanation about the progress which completed the white conductivity powder by this invention is given.

[0013] In order to give conductivity to a white inorganic pigment, how to cover directly as an approach of covering the hydrate of the indium oxide containing the hydrate of diacid-ized tin on a particle front face was examined first. However, good conductivity was not acquired, even if it could not make an inorganic pigment particle front face cover the hydrate of indium oxide with this approach to homogeneity and having been heat-treated under the effect of the inorganic pigment particle of a base. Then, in order to solve this problem, as a result of continuing examination, it became clear that a uniform coat could be formed by observation by the transmission electron microscope by covering with the form of a hydrate the metallic oxide usually used considering the front face of the inorganic pigment particle of a base as coating materials, such as an aluminum oxide, and a zinc oxide, a zirconium dioxide, and covering the hydrate of the indium oxide which contains the hydrate of diacid-ized tin succeedingly. However, these metallic oxides were still insufficient for obtaining a good conductive thing under the effect of the hydrate of a substrate. Then, as a result of making a substrate into the hydrate of the tin oxide, it becomes clear that the powder in which effect from the hydrate of the inorganic pigment particle of a base and the tin oxide of a substrate is not received, but very good conductivity is shown is obtained, and it came to complete this invention. In addition, even if the hydrate of a small amount of indium oxide is mixing into the hydrate of lower layer diacid-ized tin in the range which does not spoil the effectiveness of this invention, it does not interfere.

[0014] Detailed explanation of the manufacture approach in this invention will be given succeedingly.

[0015] There are various approaches as an approach of making the coat of the hydrate of lower layer diacid-ized tin forming. For example, after adding the solution of tin<4> salt or a stannate to the water suspension of a white inorganic pigment, the approach of adding independently in parallel the approach, the tin<4> salt or the tin hydrochloric acid which adds alkali or an acid, alkali, or an acid, and carrying out coat processing etc. is in it. for carrying out coat processing of the hydrated compound of the tin oxide on a white inorganic pigment particle front face at homogeneity -- the approach of the latter concurrency addition -- more -- suitable -- **** -- this time -- water suspension -- 50-100 degrees C -- warming -- holding is more desirable. Moreover, pH at the time of carrying out concurrency addition of tin<4> salt or a stannate, alkali, or the acid is set to 2-9. Since the isoelectric point of a diacid-ized tin hydrate is pH=5.5, it can be important to maintain pH=2-5 or pH 6-9 preferably, and, thereby, it can make a white inorganic pigment particle front face carry out the deposition of the hydration product of tin to homogeneity.

[0016] As tin<4> salt, tin chloride, sulfuric-acid tin, nitric-acid tin, etc. can be used, for example. Moreover, as a stannate, stannic-acid sodium, a stannic-acid potassium, etc. can be used, for example.

[0017] As alkali, a sodium hydroxide, a potassium hydroxide, a sodium carbonate, potassium carbonate, an ammonium carbonate, aqueous ammonia, ammonia gas, etc. can use a hydrochloric acid, a sulfuric acid, a nitric acid, an acetic acid, etc. as an acid, for example.

[0018] The amount of coats of the hydrate of diacid-ized tin is 0.5 - 50 % of the weight as SnO2 to the white inorganic pigment of a base, and is 1.5 - 40 % of the weight preferably. If too few, the coat condition of the hydrate of the indium oxide containing the tin oxide covered upwards becomes uneven, and moreover, the volume resistivity of fine particles will become high in response to the effect of the inorganic pigment of a base. If many [too], the amount of the hydrate of the tin oxide which has not been stuck to the inorganic pigment particle front face of a base will increase, and a coat will tend to become an ununiformity.

[0019] Next, although the approach of making the coat of the hydrate of the indium oxide containing the upper diacid-ized tin forming also has various approaches, in order not to dissolve the coat of the hydrate of the diacid-ized tin covered previously, the method of adding independently the mixed solution and alkali of tin<4> salt and an indium salt in parallel, and making a coat form is more desirable. At this time, it is more desirable to warm water suspension at 50-100 degrees C. Moreover, pH at the time of carrying out concurrency addition of a mixed solution and the alkali is set to 2-9, it can be important to maintain by pH 2-5 or pH 6-9 preferably, and, thereby, it can carry out the deposition of tin and the hydration product of an indium to homogeneity.

[0020] As a raw material of tin, tin chloride, sulfuric-acid tin, nitric-acid tin, etc. can be used, for example. As a raw material of an indium, indium chloride, indium sulfate, etc. can be used, for example.

[0021] To In 2O3, even if a diacid-ized tin addition is 2.5 - 15 % of the weight preferably 0.1 to 20% of the weight as SnO2, and there are and there are, desired conductivity is not acquired. [too many] [too few]

[0022] Even if desired conductivity will not be acquired to the inorganic pigment of a base if it is 8 - 150 % of the weight preferably five to 200% of the weight and is too few as In 2O3, but there are too many throughputs of indium oxide, conductivity hardly improves, and becomes expensive and is not desirable from a cost side.

[0023] In addition, in this detail, "conductive" powder means what has the value of 1 - 500 ohm-cm as a volume resistivity value of fine particles. As the example mentioned later is shown, the white conductivity powder which says 100 or less ohm-cm comparable as an antimony content article by this invention, and it says is 10 or less ohm-cm by the case and which was dramatically excellent in conductivity can be obtained.

[0024] In case it heat-treats, it is desirable to carry out according to a non-oxidizing atmosphere at 350-750 degrees C, and it can make low triple [2-] figures volume resistivity of fine particles compared with what was heat-treated in air.

[0025] Inert gas can be used in order to consider as a non-oxidizing atmosphere. As inert gas, nitrogen, helium, an argon, carbon dioxide gas, etc. can be used. Heat-treating industrially, blowing nitrogen gas is advantageous in cost, and that by which the property was stabilized is obtained.

[0026] Preferably, the temperature at the time of heating is 400-700 degrees C, and 350-750 degrees C of desired conductivity cannot acquire it easily, also when lower [than this range] and high. Moreover, since heating time cannot desire effectiveness beyond it even if there is no heating effectiveness and it is too long, when too brief, 15 minutes - about 4 hours are suitable for it, and it is about 1 - 2 hours preferably.

[0027] An example is given to below and this invention is further explained to a detail. The following examples are not described only for instantiation and the range of invention is not restricted by these.

[0028] 1l. of water was made to distribute 100g (Titan Kogyo KR-310 and specific-surface-area [of 7m] 2/g) of example 1 rutile titanium dioxides, and it considered as water suspension. this suspension -- 70 degrees C -- warming -- it held. It applied for about 40 minutes and simultaneous adding of the solution and 12-% of the weight aqueous ammonia which melted 11.6g (SnCl4and5H2O) of stannic chlorides

prepared separately to 100ml of 2-N hydrochloric acids was carried out for pH of suspension so that it might hold to 7-8. Simultaneous dropping of the solution and 12-% of the weight aqueous ammonia which melted 36.7g (InCl3) of indium chloride and 5.4g (SnCl4and5H2O) of stannic chlorides prepared separately succeedingly to 450ml of 2-N hydrochloric acids was carried out over about 1 hour so that pH of suspension might be held to 7-8. After dropping termination, processing suspension was filtered, it washed, and the cake of the obtained processing pigment was dried at 110 degrees C.

[0029] Subsequently, the obtained desiccation powder was heat-treated at 500 degrees C in the nitrogen gas air current (a part for 1l./) for 1 hour, and the white conductivity powder made into the object was obtained.

[0030] Powdered volume resistivity was 3.9 ohm-cm. Moreover, the coat condition on the front face of a particle was very uniform as shown in the transmission electron microscope photograph of (drawing 1).

[0031] In example 2 example 1, instead of the rutile titanium dioxide, the aluminum oxide (Sumitomo Chemical AKP-30 and specific-surface-area [of 6m] 2/g) was used, and 11.6g of stannic chlorides was set to 16.2g, and also it processed like the case of this example, and the white conductivity powder made into the object was obtained. The volume resistivity of fine particles was 8.2 ohm-cm.

[0032] In example 3 example 1, the zinc oxide (Mitsui Mining & Smelting zinc white) was used instead of the rutile titanium dioxide, and the white conductivity powder which 16.2g, 36.7g of indium chloride, and 5.4g of stannic chlorides were set to 51.3g and 13.3g, respectively, and also processes 11.6g of stannic chlorides like the case of this example, and targets them was obtained. The volume resistivity of fine particles was 39 ohm-cm.

[0033] In example 4 example 1, the white conductivity powder which used the barium sulfate (product B-50 made from the Sakai chemistry) instead of the rutile titanium dioxide, and 36.7g of indium chloride and 5.4g of stannic chlorides were set to 23.2g and 4.7g, respectively, and also processes like the case of this example, and is made into the object was obtained. The volume resistivity of fine particles was 47 ohm-cm.

[0034] In example 5 example 1, potassium titanate (Titan Kogyo HT-300 and specific-surface-area [of 3m] 2/g) was used instead of the rutile titanium dioxide, 36.7g of indium chloride and 5.4g of stannic chlorides were set to 31.9g and 4.7g at 6.0g, respectively, and also 11.6g of stannic chlorides was processed like the case of this example, and the white conductivity powder made into the object was obtained. The volume resistivity of fine particles was 87 ohm-cm.

[0035] In example 6 example 1, an anatase mold ultrafine particle titanium dioxide (Titan Kogyo STT-65C and specific-surface-area 60m2/g) is used instead of a rutile titanium dioxide. The solution which melted 11.6g of stannic chlorides to 100ml of 2-N hydrochloric acids In the solution which melted 39.8g of stannic chlorides to 300ml of 2-N hydrochloric acids Moreover, the solution which melted 36.7g of indium chloride, and 5.4g of stannic chlorides to 450ml of 2-N hydrochloric acids It considered as the solution which melted 159.6g of indium chloride, and 23.5g of stannic chlorides to 1000ml of 2-N hydrochloric acids, and also it processed like the case of this example, and the white conductivity powder made into the object was obtained. The volume resistivity of fine particles was 42 ohm-cm.

[0036] In example 7 example 1, everything but having used the muscovite (Kuraray SUZORAITO mica and specific-surface-area 7m2/g) instead of the rutile titanium dioxide was processed like the case of this example, and obtained the white conductivity powder made into the object. The volume resistivity of fine particles was 22 ohm-cm.

[0037] example 8 example 1 -- setting -- instead of [of a rutile titanium dioxide] -- a zirconium dioxide (the high intensity zirconia made from Oriental soda --) Specific-surface-area of 17m 2/g is used. 11.6g of stannic chlorides to 23.2g Moreover, the solution which melted 36.7g of indium chloride, and 5.4g of stannic chlorides to 450ml of 2-N hydrochloric acids It considered as the solution which melted 73.4g of indium chloride, and 10.8g of stannic chlorides to 900ml of 2-N hydrochloric acids, and also it processed like the case of this example, and the white conductivity powder made into the object was obtained. The

volume resistivity of fine particles was 32 ohm-cm.

[0038] In example of comparison 1 example 1, except not performing processing with the solution which melted 11.6g of stannic chlorides to 100ml of 2-N hydrochloric acids, it processed like the case of this example and white conductivity powder was obtained. The volume resistivity of fine particles was dramatically as high as 3.9x105 ohm-cm, and there was much what separated from the base like the transmission electron microscope photograph which also showed the coat condition on the front face of a particle to (drawing 2).

[0039] In example of comparison 2 example 1, everything but carrying out in air instead of heat-treating in a nitrogen gas air current was processed like the case of this example, and obtained white powder. The volume resistivity of fine particles was very as high as 4.3x103 ohm-cm.

[0040]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is a transmission electron microscope photograph (x120,000) showing the particulate structure of the white conductivity powder obtained in the example 1.

[Drawing 2] It is a transmission electron microscope photograph (x120,000) showing the particulate structure of the white conductivity powder obtained in the example 1 of a comparison.

DRAWINGS

[Drawing 1]

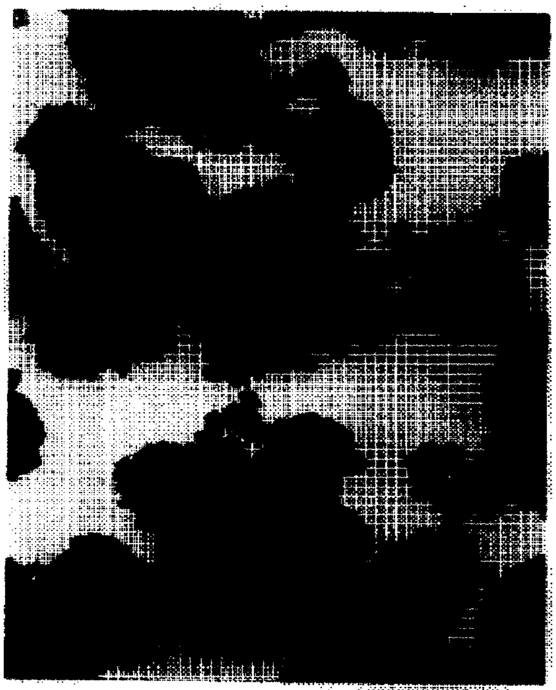
図面代用写真

X 120,000

写真

[Drawing 2]

図面代用写真



×120,000

写真

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最終頁に続く

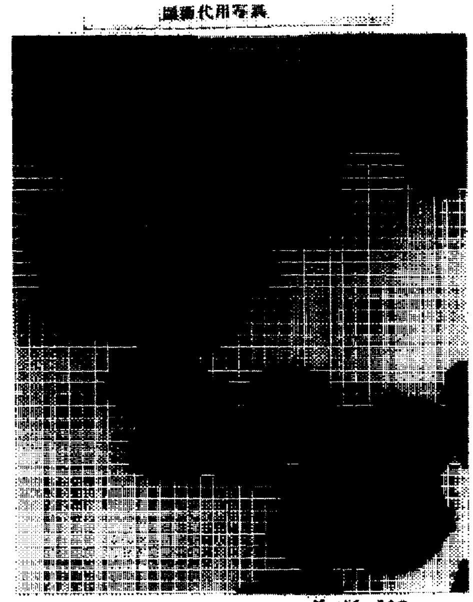
(54)【発明の名称】　白色導電性粉末およびその製造方法

(57)【要約】

【目的】　体積固有抵抗が極めて低く、白度が極めて高く、しかも、毒性上の問題のあるアンチモンを含有しない、白色導電性粉末を提供することを目的とする。

【構成】　本発明は白色無機顔料粒子表面に下層に二酸化スズ層、上層に二酸化スズを含有する酸化インジウム層の二重の導電性被覆層を有することを特徴とする白色導電性粉末を提供する。本発明にかかる白色導電性粉末は、白色無機顔料粒子表面へ、まずスズの加水反応生成物を均一に沈着させ、引き続き二酸化スズを０．１～２０重量％含む酸化インジウムの水和物を被覆させ、さらに非酸化性雰囲気にて３５０～７５０℃で加熱処理することにより得られる。

図面代用写真



写　真

【特許請求の範囲】

【請求項１】　白色無機顔料粒子の表面に、下層が二酸化スズの層であり、上層が二酸化スズを含む酸化インジウムの層である導電性被覆層を有することを特徴とする白色導電性粉末。

【請求項２】　白色無機顔料粒子が二酸化チタン、酸化アルミニウム、二酸化ケイ素、酸化亜鉛、硫酸バリウム、酸化ジルコニウム、チタン酸アルカリ金属塩及び白雲母からなる群より選ばれる請求項１記載の白色導電性粉末。

【請求項３】　白色無機顔料粒子表面へ、二酸化スズの水和物を顔料に対して、SnO_2として０．５～５０重量％被覆させ、次いで二酸化スズの水和物をSnO_2として０．１～２０重量％含有する酸化インジウムの水和物を顔料に対してIn_2O_3として５～２００重量％被覆させ、さらに、非酸化性雰囲気にて３５０～７５０℃で加熱処理することを特徴とする請求項１記載の白色導電性粉末の製造方法。

【請求項４】　加熱処理を不活性ガスを吹き込みながら行うことを特徴とする請求項３記載の白色導電性粉末の製造方法。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明は帯電防止用の塗料・プラスチック・繊維などや、電子写真用のトナーの帯電調整剤・感光ドラムの抵抗調整剤など多分野で用いられる白色導電性粉末に関するものである。

【０００２】

【従来の技術】現在、導電材料として多量に使用されているカーボンブラックや金属粉は、体積固有抵抗が非常に低く、特性的には優れているものの、それらの色調が黒色のため用途が限定されていた。その対策として、二酸化チタンの表面を、酸化第二スズで被覆したもの（特開昭５３－９２８５４公報）やその導電性改良品としてアンチモンをドープした酸化スズを被覆した白色の導電性酸化チタンの製造法が開示された（特開昭５８－２０９００２公報など）。

【０００３】この白色導電性酸化チタンを用いた、帯電防止用の塗料、プラスチック、繊維は、白色という利点を生かし、清潔感を必要とする白衣やクリーンルームの内装あるいは明彩色の塗料やプラスチック製品に近年需要を増してきている。

【０００４】しかしながら、最近アンチモンの毒性上の問題が取沙汰されるようになり、アンチモンを含有しない白色導電性粉末の開発が必要となった。アンチモンを使用しない製法として、例えば特開平４－１５４６２１公報が開示されたが、この方法ではアンチモンを含有しないものの体積固有抵抗がアンチモンを含有したものと同等のものは得られていない。

【０００５】また、特開昭６１－１４１６１８公報では二酸化スズを含む酸化インジウムで被覆したチタン酸カリウムが開示されたが、塩化インジウムの水溶液と塩化第一スズのエタノール溶液を別途使用するので、両者の被覆割合が均一にならないため、体積固有抵抗が安定しないという問題があった。更に、基体のチタン酸カリウム粒子表面への酸化インジウムの被覆状態が悪く、かつ、基体が被覆層の導電性を低下させる不純物として作用するので、二酸化スズを含む酸化インジウムの被覆量を多くしたにもかかわらず粉体の体積固有抵抗は、１０^{4}Ω・ｃｍと高いものであった。

【０００６】また、特開昭６０－２５３１１２公報では、二酸化スズを含む酸化インジウムで被覆した白雲母が開示されたが、チタン酸カリウムの場合と同様、酸化インジウムの被覆状態が悪く、基体の影響もあって二酸化スズを含む酸化インジウムの被覆量を多くする必要があった。

【０００７】その他の白色無機顔料粒子においても二酸化スズを含む酸化インジウムの被覆を均一に被覆させることが難しく、また、基体の無機顔料粒子の影響により、体積固有抵抗を低下させることができないため導電性の良好な白色導電性粉末は得られていなかった。

【０００８】

【発明が解決しようとする課題】本発明は毒性の問題のあるアンチモンを使用しないにもかかわらず、白度が高く、かつ優れた導電性を有する、白色導電性粉末を提供しようとするものである。

【０００９】

【課題を解決するための手段】本発明者らは白度を保ちながら、かつ毒性の問題のあるアンチモンを使用しないにもかかわらず、アンチモン含有品と同等の導電性を有する白色粉末を開発する為鋭意研究を重ねた結果、本発明を完成したものである。すなわち、本発明は、白色無機顔料粒子表面に、下層が二酸化スズの層であり、上層が二酸化スズを含む酸化インジウムの層である導電性被覆層を有することを特徴とする白色導電性粉末を提供するものである。

【００１０】本発明にかかる白色導電性粉末は、白色無機顔料粒子表面に顔料に対してSnO_2として０．５～５０重量％の二酸化スズの水和物を均一に被覆させ引き続き、二酸化スズの水和物をSnO_2として０．１～２０重量％含む酸化インジウムの水和物をIn_2O_3として顔料に対して５～２００重量％被覆させ、さらに非酸化性雰囲気にて３５０～７５０℃で加熱処理することにより得られる。

【００１１】本発明の基体となる白色無機顔料粒子は市販の二酸化チタン、酸化アルミニウム、二酸化ケイ素、酸化亜鉛、硫酸バリウム、酸化ジルコニウム、チタン酸アルカリ金属塩あるいは白雲母であれば、いずれでも使用できる。二酸化チタンを例にとりより詳細に説明すると、粒子の大きさには制限がなく、また球状、針状など

の様な形状のものでも、更には結晶形として、アナターゼ型、ルチル型及び非晶質のものも使用することができる。なお本発明は白色を重視したが、酸化鉄など種々の有色顔料にも応用できる。

【００１２】次に本発明による白色導電性粉末を完成させた経過についての説明を行う。

【００１３】白色無機顔料に導電性を付与するため、粒子表面に二酸化スズの水和物を含む酸化インジウムの水和物を被覆する方法として直接被覆する方法を始めに検討した。しかしながら、この方法では無機顔料粒子表面に酸化インジウムの水和物を均一に被覆させることができず、また、基体の無機顔料粒子の影響により、加熱処理しても良好な導電性が得られなかった。そこで、この問題を解決するため、検討を続けた結果、基体の無機顔料粒子の表面を酸化アルミニウム、酸化亜鉛や酸化ジルコニウム等のコーティング材として通常用いられている金属酸化物を水和物の形で被覆し、引き続き二酸化スズの水和物を含む酸化インジウムの水和物を被覆することにより、透過型電子顕微鏡による観察で均一な被膜が形成できることが判明した。但し、これらの金属酸化物では下地の水和物の影響により良好な導電性のものを得るにはまだ不十分であった。そこで下地を酸化スズの水和物とした結果、基体の無機顔料粒子及び下地の酸化スズの水和物からの影響を受けず非常に良好な導電性を示す粉末が得られることが判明し、本発明を完成するに至った。なお、下層の二酸化スズの水和物の中に、本発明の効果を損なわない範囲で、少量の酸化インジウムの水和物が混入していてもさしつかえない。

【００１４】本発明における製造方法の詳細な説明を引き続き行うことにする。

【００１５】下層の二酸化スズの水和物の被膜を形成させる方法としては、種々の方法がある。例えば、白色無機顔料の水懸濁液に、スズ塩またはスズ酸塩の溶液を添加した後、アルカリまたは酸を添加する方法、スズ塩またはスズ塩酸とアルカリまたは酸とを別々に並行して添加し被覆処理する方法等がある。白色無機顔料粒子表面に酸化スズの含水物を均一に被覆処理するには、後者の並行添加の方法がより適しており、この時、水懸濁液を５０～１００℃に加温保持することがより好ましい。又、スズ塩またはスズ酸塩とアルカリまたは酸とを並行添加する際のｐＨを２～９とする。二酸化スズ水和物の等電点はｐＨ＝５．５であるので、好ましくはｐＨ＝２～５あるいはｐＨ６～９を維持することが重要で、これによりスズの加水反応生成物を白色無機顔料粒子表面に均一に沈着させることができる。

【００１６】スズ塩としては、例えば、塩化スズ、硫酸スズ、硝酸スズ等を使用することができる。また、スズ酸塩としては、例えば、スズ酸ナトリウム、スズ酸カリウム等を使用することができる。

【００１７】アルカリとしては、例えば、水酸化ナトリウム、水酸化カリウム、炭酸ナトリウム、炭酸カリウム、炭酸アンモニウム、アンモニア水、アンモニアガス等、酸としては、例えば、塩酸、硫酸、硝酸、酢酸等を使用することができる。

【００１８】二酸化スズの水和物の被覆量は基体の白色無機顔料に対して、SnO_2として０．５～５０重量％であり、好ましくは１．５～４０重量％である。少な過ぎると、上に被覆する酸化スズを含む酸化インジウムの水和物の被覆状態が不均一となり、しかも、基体の無機顔料の影響を受け、粉体の体積固有抵抗が高くなる。多過ぎると、基体の無機顔料粒子表面に密着していない酸化スズの水和物の量が多くなり、被覆が不均一になり易い。

【００１９】次に上層の二酸化スズを含む酸化インジウムの水和物の被覆を形成させる方法も種々の方法があるが、先に被覆した二酸化スズの水和物の被膜を溶解させないため、スズ塩及びインジウム塩の混合溶液とアルカリとを別々に並行して添加し被膜を形成させる方法がより好ましい。この時、水懸濁液を５０～１００℃に加温することがより好ましい。また、混合溶液とアルカリとを並行添加する際のｐＨは２～９とし、好ましくはｐＨ２～５あるいは、ｐＨ６～９で維持することが重要で、これによりスズ及びインジウムの加水反応生成物を均一に沈着させることができる。

【００２０】スズの原料としては、例えば、塩化スズ、硫酸スズ、硝酸スズ等を使用することができる。インジウムの原料としては、例えば、塩化インジウム、硫酸インジウム等を使用することができる。

【００２１】二酸化スズ添加量は、In_2O_3に対してSnO_2として０．１～２０重量％、好ましくは、２．５～１５重量％であり、少な過ぎても、多過ぎても所望の導電性が得られない。

【００２２】酸化インジウムの処理量は基体の無機顔料に対して、In_2O_3として５～２００重量％、好ましくは８～１５０重量％であり、少な過ぎると所望の導電性が得られず、多過ぎても導電性はほとんど向上せず、また、高価になりコスト面からも好ましくない。

【００２３】なお、本明細において、「導電性」粉末とは、粉体の体積固有抵抗値として１～５００Ω・ｃｍの値を有するものを意味する。後述する実施例においても示されるように、本発明により、アンチモン含有品と同程度の１００Ω・ｃｍ以下、場合により１０Ω・ｃｍ以下という非常に導電性に優れた白色導電性粉末を得ることができる。

【００２４】加熱処理を行う際には、３５０～７５０℃で非酸化性雰囲気にて行うことが好ましく、空気中で加熱処理したものと比べると粉体の体積固有抵抗を２～３桁低くすることができる。

【００２５】非酸化性雰囲気とするためには、不活性ガスが使用できる。不活性ガスとしては例えば、窒素、ヘ

リウム、アルゴン、炭酸ガス等を使用することができる。工業的には、窒素ガスを吹き込みながら加熱処理を行うことがコスト的に有利であり、特性の安定したものが得られる。

【0026】加熱する際の温度は350～750℃、好ましくは400～700℃であり、この範囲より低い場合にも、高い場合にも、所望の導電性が得がたい。また、加熱時間は、短かすぎる場合には加熱効果がなく、長すぎてもそれ以上の効果が望めないことから、15分～4時間程度が適当であり、好ましくは、1～2時間程度である。

【0027】以下に実施例を挙げて本発明をさらに詳細に説明する。以下の実施例は単に例示のために記すものであり、発明の範囲が、これらによって制限されるものではない。

【0028】実施例1

ルチル型二酸化チタン（チタン工業製ＫＲ－３１０，比表面積７m^2/ｇ）１００ｇを水１リットルに分散させて水懸濁液とした。この懸濁液を７０℃に加温保持した。別途用意した塩化第二スズ（$SnCl_4 \cdot 5H_2O$）１１．６ｇを２Ｎ塩酸１００ミリリットルに溶かした溶液と１２重量％アンモニア水とを、懸濁液のｐＨを７～８に保持するように約４０分かけ同時添加した。引き続き別途用意した塩化インジウム（$InCl_3$）３６．７ｇおよび塩化第二スズ（$SnCl_4 \cdot 5H_2O$）５．４ｇを２Ｎ塩酸４５０ミリリットルに溶かした溶液と１２重量％アンモニア水とを懸濁液のｐＨを７～８に保持する様に約１時間かけて同時滴下した。滴下終了後、処理懸濁液を濾過、洗浄し、得られた処理顔料のケーキを１１０℃で乾燥した。

【0029】次いで得られた乾燥粉末を窒素ガス気流中（１リットル／分）で５００℃にて１時間熱処理して、目的とする白色導電性粉末を得た。

【0030】粉末の体積固有抵抗は３．９Ω・ｃｍであった。また、粒子表面の被覆状態は（図１）の透過型電子顕微鏡写真に示す様に非常に均一なものであった。

【0031】実施例2

実施例１において、ルチル型二酸化チタンの代わりに、酸化アルミニウム（住友化学工業製ＡＫＰ－３０，比表面積６m^2/ｇ）を用い、塩化第二スズ１１．６ｇを１６．２ｇとしたほかは同例の場合と同様に処理して、目的とする白色導電性粉末を得た。粉体の体積固有抵抗は８．２Ω・ｃｍであった。

【0032】実施例3

実施例１において、ルチル型二酸化チタンの代わりに酸化亜鉛（三井金属製亜鉛華）を用い、塩化第二スズ１１．６ｇを１６．２ｇ、塩化インジウム３６．７ｇおよび塩化第二スズ５．４ｇを夫々５１．３ｇおよび１３．３ｇとしたほかは同例の場合と同様に処理して、目的とする白色導電性粉末を得た。粉体の体積固有抵抗は３９Ω・ｃｍであった。

【0033】実施例4

実施例１において、ルチル型二酸化チタンの代わりに硫酸バリウム（堺化学製Ｂ－５０）を用い、塩化インジウム３６．７ｇおよび塩化第二スズ５．４ｇを夫々２３．２ｇおよび４．７ｇとしたほかは、同例の場合と同様に処理して目的とする白色導電性粉末を得た。粉体の体積固有抵抗は４７Ω・ｃｍであった。

【0034】実施例5

実施例１において、ルチル型二酸化チタンの代わりにチタン酸カリウム（チタン工業製ＨＴ－３００，比表面積３m^2/ｇ）を用い、塩化第二スズ１１．６ｇを6.0ｇに、塩化インジウム３６．７ｇおよび塩化第二スズ５．４ｇを夫々３１．９ｇおよび４．７ｇとしたほかは、同例の場合と同様に処理して、目的とする白色導電性粉末を得た。粉体の体積固有抵抗は８７Ω・ｃｍであった。

【0035】実施例6

実施例１において、ルチル型二酸化チタンの代わりにアナターゼ型超微粒子二酸化チタン（チタン工業製ＳＴＴ－６５Ｃ，比表面積６０m^2/ｇ）を用い、塩化第二スズ１１．６ｇを２Ｎ塩酸１００ミリリットルに溶かした溶液を、塩化第二スズ３９．８ｇを２Ｎ塩酸３００ミリリットルに溶かした溶液に、又、塩化インジウム３６．７ｇおよび塩化第二スズ５．４ｇを２Ｎ塩酸４５０ミリリットルに溶かした溶液を、塩化インジウム１５９．６ｇおよび塩化第二スズ２３．５ｇを２Ｎ塩酸１０００ミリリットルに溶かした溶液としたほかは、同例の場合と同様に処理して、目的とする白色導電性粉末を得た。粉体の体積固有抵抗は４２Ω・ｃｍであった。

【0036】実施例7

実施例１において、ルチル型二酸化チタンの代わりに白雲母（クラレ製スゾライトマイカ，比表面積７m^2/ｇ）を用いたことのほかは同例の場合と同様に処理して、目的とする白色導電性粉末を得た。粉体の体積固有抵抗は２２Ω・ｃｍであった。

【0037】実施例8

実施例１において、ルチル型二酸化チタンの代わりに酸化ジルコニウム（東洋曹達製高強度ジルコニア、比表面積１７m^2/ｇ）を用い、塩化第二スズ１１．６ｇを２３．２ｇに、又、塩化インジウム３６．７ｇおよび塩化第二スズ５．４ｇを２Ｎ塩酸４５０ミリリットルに溶かした溶液を、塩化インジウム７３．４ｇおよび塩化第二スズ１０．８ｇを２Ｎ塩酸９００ミリリットルに溶かした溶液としたほかは、同例の場合と同様に処理して、目的とする白色導電性粉末を得た。粉体の体積固有抵抗は３２Ω・ｃｍであった。

【0038】比較例1

実施例１において、塩化第二スズ１１．６ｇを２Ｎ塩酸１００ミリリットルに溶かした溶液での処理を行わないこと以外は、同例の場合と同様に処理して、白色導電性

粉末を得た。粉体の体積固有抵抗は３．９×１０^{5}Ω・ｃｍと非常に高く、粒子表面の被覆状態も（図２）に示した透過型電子顕微鏡写真の様に基体より遊離したものが多いものであった。

【００３９】比較例２

実施例１において、熱処理を窒素ガス気流中で行う代わりに空気中で行うことのほかは、同例の場合と同様に処理して白色粉末を得た。粉体の体積固有抵抗は４．３×１０^{3}Ω・ｃｍと非常に高いものであった。

【００４０】

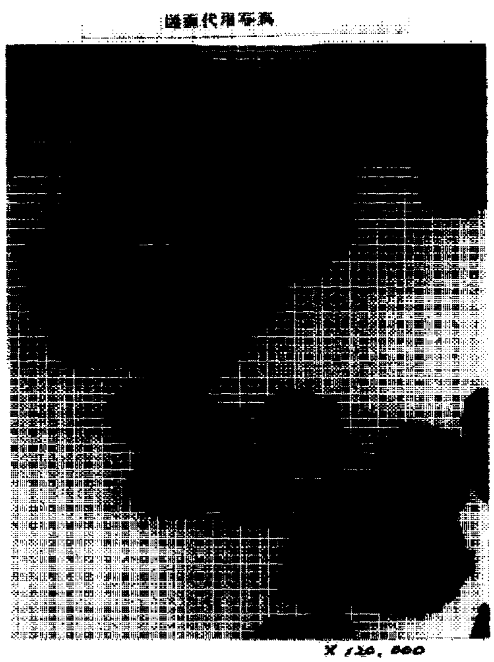
【発明の効果】本発明は毒性上の問題のあるアンチモンを使用することなく種々の分野に利用できる導電性に優れた白色度の高い導電性粉末を、比較的容易に製造するものであり、工業的に高い利点がある。

【図面の簡単な説明】

【図１】実施例１で得られた白色導電性粉末の粒子構造を表す透過型電子顕微鏡写真（×120,000）である。

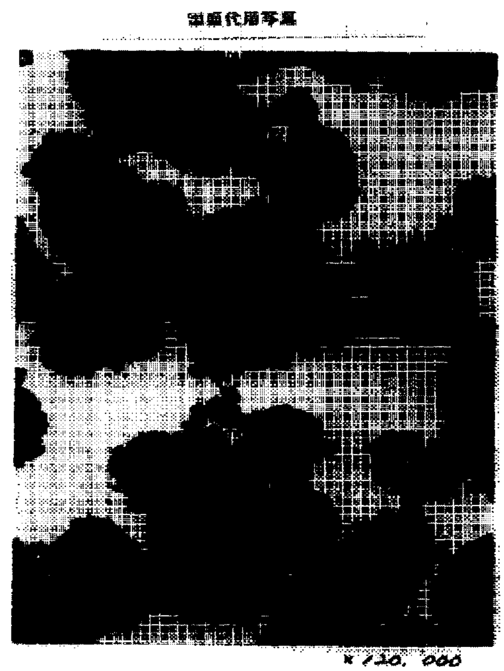
【図２】比較例１で得られた白色導電性粉末の粒子構造を表す透過型電子顕微鏡写真（×120,000）である。

【図１】



写　真

【図２】



写　真

フロントページの続き

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